CHM225 - PROBLEM SET # 4

Q1. $\hat{L}_x = y\hat{p}_z - z\hat{p}_y$

$\hat{L}_y = z\hat{p}_x - x\hat{p}_z$

$\hat{L}_z = x\hat{p}_y - y\hat{p}_x$

a) $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

$$= (y\hat{p}_z - z\hat{p}_y)(y\hat{p}_z - z\hat{p}_y) + (z\hat{p}_x - x\hat{p}_z)(z\hat{p}_x - x\hat{p}_z) + (x\hat{p}_y - y\hat{p}_x)(x\hat{p}_y - y\hat{p}_x)$$

$$\cancel{= y^2\hat{p}_z^2 - yz\hat{p}_z\hat{p}_y - zy\hat{p}_y\hat{p}_z + z^2\hat{p}_y^2 + z^2\hat{p}_x^2 - zx\hat{p}_x\hat{p}_z - xz\hat{p}_z\hat{p}_x + x^2\hat{p}_z^2 + x^2\hat{p}_y^2 - xy\hat{p}_y}$$

$$\cancel{= y^2\hat{p}_z^2 - y\hat{p}_z z\hat{p}_y - z\hat{p}_y y\hat{p}_z + z^2\hat{p}_y^2 + z^2\hat{p}_x^2 - zx\hat{p}_x\hat{p}_z}$$

$$= y^2\hat{p}_z^2 - y\hat{p}_z z\hat{p}_y - z\hat{p}_y y\hat{p}_z + z^2\hat{p}_y^2 + z^2\hat{p}_x^2 - z\hat{p}_x x\hat{p}_z - x\hat{p}_z z\hat{p}_x + x^2\hat{p}_z^2$$

$$+ x^2\hat{p}_y^2 - x\hat{p}_y y\hat{p}_x - y\hat{p}_x x\hat{p}_y + y^2\hat{p}_x^2$$

1(e) $\quad [\hat{L}_x, \hat{L}_y]$

$$= [y\hat{p}_z - z\hat{p}_y, z\hat{p}_x - x\hat{p}_z]$$

NOTE: $[A+B, C]$

$$\equiv (A+B)C - C(A+B) \quad \text{by definition}$$
$$= AC + BC - CA + CB$$
$$= (AC - CA) + (BC - CB)$$
$$= [A, C] + [B, C]$$

$$[A+B, C] = [A, C] + [B, C]$$

<u>Similarly</u>:

$$[A, B+C] = [A, B] + [A, C]$$

$$\Rightarrow \quad [\hat{L}_x, \hat{L}_y] = [y\hat{p}_z, z\hat{p}_x - x\hat{p}_y] - [z\hat{p}_y, z\hat{p}_x - x\hat{p}_y]$$

$$= \underbrace{[y\hat{p}_z, z\hat{p}_x]}_{①} - \underbrace{[y\hat{p}_z, x\hat{p}_z]}_{②} - \underbrace{[z\hat{p}_y, z\hat{p}_x]}_{③} + \underbrace{[z\hat{p}_y, x\hat{p}_z]}_{④}$$

We evaluate each of the 4 terms of the expansion in turn.

② $[y\hat{p}_z, x\hat{p}_z] = 0$ (Notice all ~~four~~ operators x, y, p_z commute with each other)

③ $[z\hat{p}_y, z\hat{p}_x] = 0$ 〃

④ $[z\hat{p}_y, x\hat{p}_z] = z[\hat{p}_y, x\hat{p}_z] + [z, x\hat{p}_z]\hat{p}_y$

$= zx\cancel{[\hat{p}_y, \hat{p}_z]} + z\cancel{[\hat{p}_y, x]}\hat{p}_z + x[z, \hat{p}_z]\hat{p}_y + \cancel{[z, x]}\hat{p}_z\hat{p}_y$

$= i\hbar x\hat{p}_y$

$\Rightarrow [\hat{L}_x, \hat{L}_y] = i\hbar x\hat{p}_y - i\hbar y\hat{p}_x$

$= i\hbar(x\hat{p}_y - y\hat{p}_x)$

$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$

1(b) $[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$

$= \underbrace{[\hat{L}_x^2, \hat{L}_x]}_{①} + \underbrace{[\hat{L}_y^2, \hat{L}_x]}_{②} + \underbrace{[\hat{L}_z^2, \hat{L}_x]}_{③}$

NOTE. $[AB, C] = (AB)C - C(AB)$ by definition

$= A(BC) - (CA)B$ (multiplication is associative)

$= A(BC) - ACB + ACB - (CA)B$

Add & Subtract ACB

$= A(BC) - A(CB) + (AC)B - (CA)B$

$= A(BC - CB) + (AC - CA)B$

$= A[B, C] + [A, C]B$

Thus: $[AB, C] = A[B, C] + [A, C]B$

Similarly $[A, BC] = B[A, C] + [A, B]C$

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①

$\Rightarrow [y\hat{p}_z, z\hat{p}_x] = y[\hat{p}_z, z\hat{p}_x] + [y, z\hat{p}_x]\hat{p}_z$

$= \cancel{yz[\hat{p}_z, \hat{p}_x]} + y[\hat{p}_z, z]\hat{p}_x + \cancel{z[y, \hat{p}_x]\hat{p}_z} + \cancel{[y, z]\hat{p}_x\hat{p}_z}$

recall $[\hat{p}_z, z] = -i\hbar$

$\Rightarrow [y\hat{p}_z, z\hat{p}_y] = -i\hbar y\hat{p}_x$

① $[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x \cancel{[\hat{L}_x, \hat{L}_x]} + \cancel{[\hat{L}_x, \hat{L}_x]} \hat{L}_x$

$= 0$

② $[\hat{L}_y^2, \hat{L}_x] = \hat{L}_y [\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x] \hat{L}_y$

$= \hat{L}_y(-i\hbar \hat{L}_z) + (-i\hbar \hat{L}_z)\hat{L}_y$

$= -i\hbar(\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y)$

③ $[\hat{L}_z^2, \hat{L}_x] = \hat{L}_z [\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x] \hat{L}_z$

$= \hat{L}_z(i\hbar \hat{L}_y) + (i\hbar \hat{L}_y)\hat{L}_z$

$= i\hbar(\hat{L}_z \hat{L}_y + \hat{L}_y \hat{L}_z)$

$\Rightarrow [\hat{L}^2, \hat{L}_x] = -i\hbar[\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y] + i\hbar[\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y]$

$= 0$

1c) $[\hat{L}^2, \hat{L}_y] = 0$ by symmetry with previous problem.

1d) $[\hat{L}^2, \hat{L}_z] = 0$ "

Q2. a) Energy Difference Harmonic Oscillator.

$$E_k = \hbar\omega\left(k+\frac{1}{2}\right) \qquad k = 0, 1, 2 \ldots$$

consider $j \longrightarrow k$ transition

$$\Delta E_{jk} = E_k - E_j$$
$$= \hbar\omega\left(k+\frac{1}{2}\right) - \hbar\omega\left(j+\frac{1}{2}\right)$$
$$= \hbar\omega(k-j)$$

since j, k can take any non-negative integer values

therefore

$\Delta E = n\hbar\omega$, where $n = (k-j)$ is an integer.

b). the particle on a ring

$$E_k = \frac{\hbar^2 k^2}{2mr^2} \qquad k = 0, \pm1, \pm2 \ldots$$

$$\Delta E_{jk} = E_k - E_j$$
$$= \frac{\hbar^2 k^2}{2mr^2} - \frac{\hbar^2 j^2}{2mr^2}$$
$$= \frac{\hbar^2}{2mr^2}\left(k^2 - j^2\right) \qquad \text{where } j \,\&\, k \text{ are integers.}$$

2c) the particle in a 3-dimensional box.

$$E_k = \frac{\hbar^2\pi^2}{2m}\left(\left(\frac{k_x}{L_x}\right)^2 + \left(\frac{k_y}{L_y}\right)^2 + \left(\frac{k_z}{L_z}\right)^2\right)$$

where k_x, k_y, k_z are non-zero integers.

$$\Delta E_{jk} = E_k - E_j$$

$$= \frac{\hbar^2\pi^2}{2m}\left(\left(\frac{k_x}{L_x}\right)^2 + \left(\frac{k_y}{L_y}\right)^2 + \left(\frac{k_z}{L_y}\right)^2\right) - \frac{\hbar^2\pi^2}{2m}\left(\left(\frac{j_x}{L_x}\right)^2 + \left(\frac{j_y}{L_y}\right)^2 + \left(\frac{j_z}{L_z}\right)^2\right)$$

$$= \frac{\hbar^2\pi^2}{2m}\left(\frac{k_x^2 - j_x^2}{L_x^2} + \frac{k_y^2 - j_y^2}{L_y^2} + \frac{k_z^2 - j_z^2}{L_z^2}\right)$$

k_x, k_y, k_z & j_x, j_y, j_z } non-neg integers.

2d). the hydrogen atom.

$$E_k = -\frac{Z^2e^2}{8\pi\varepsilon_0 a k^2}$$

$$\Rightarrow \Delta E_{jk} = E_k - E_j$$

$$= -\frac{Z^2e^2}{8\pi\varepsilon_0 a k^2} - \left(\frac{Z^2e^2}{8\pi\varepsilon_0 a j^2}\right)$$

$$= \frac{Ze^2}{8\pi\varepsilon_0 a}\left(\frac{1}{j^2} - \frac{1}{k^2}\right)$$

j & k are non-negative integers.

Q3. a) Two particles. Four possible spins.

$$\phi_1(1,2) = \alpha(1)\alpha(2)$$
$$\phi_2(1,2) = \alpha(1)\beta(2)$$
$$\phi_3(1,2) = \beta(1)\alpha(2)$$
$$\phi_4(1,2) = \beta(1)\beta(2)$$

b) Interchange particles:

$$\phi_1(2,1) = \alpha(2)\alpha(1) = \alpha(1)\alpha(2) = \phi_1(1,2)$$
$$\phi_2(2,1) = \alpha(2)\beta(1) = \beta(1)\alpha(2) = \phi_3(1,2)$$
$$\phi_3(2,1) = \beta(2)\alpha(1) = \alpha(1)\beta(2) = \phi_2(1,2)$$
$$\phi_4(2,1) = \beta(2)\beta(1) = \beta(1)\beta(2) = \phi_4(1,2)$$

c) Symmetric spin states

$$\psi_1^s(1,2) = \phi_1(1,2) = \alpha(1)\alpha(2)$$
$$\psi_2^s(1,2) = \phi_4(1,2) = \beta(1)\beta(2)$$
$$\psi_3^s(1,2) = \phi_2(1,2) + \phi_3(1,2)$$
$$= \alpha(1)\beta(2) + \beta(1)\alpha(2)$$

d) Anti-symmetric spin states.

$$\psi^{A}(1,2) = \phi_{2}(1,2) - \phi_{3}(1,2)$$
$$= \alpha(1)\beta(2) - \beta(1)\alpha(2)$$

e) let χ represent the spatial wavefunction of the two spin ½ particles. The total spatial wavefunction of the 2 particles is symmetric

$$\Theta(1,2) = \chi(1)\chi(2) = \chi(2)\chi(1) = \Theta(2,1).$$

Since the total wavefunction of spin ½ particles (fermions) must be anti-symmetric with respect to exchange of particle indices this allows only one possibility.

$$\underbrace{\Psi(1,2) = \underbrace{\left[\chi(1)\chi(2)\right]}_{\text{symmetric}}\underbrace{\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\text{anti-symmetric}}}_{\text{anti- symmetric.}}$$

NOTE: $\Psi(2,1) = -\Psi(1,2)$.

Q4. $\hat{H} = \hat{H}_1 \cancel{+} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1}$

a) why is m_e a good approximation for the reduced mass μ.

The reduced mass of the Helium ion

$M \equiv$ mass of Helium nucleus $= 4m_p$

$\cancel{\mu = \frac{M+m_e}{Mm_e}}$

$m_e \equiv$ mass of electron

$$\mu = \frac{M \cdot m_e}{M + m_e} \qquad M \gg m_e \quad (M \simeq 4\times10^3 m_e).$$

$$\simeq \frac{M \cdot m_e}{M} = m_e$$

b). Ground state wavefunctions:

$$\psi_g(1) = 1s'_{He}\alpha(1) \quad \text{or} \quad 1s'_{He}\beta(1)$$

$$= \frac{1}{\sqrt{\pi}}\left(\frac{2}{a}\right)^{3/2} e^{-2r/a}\alpha(1) \quad \text{or} \quad \frac{1}{\sqrt{\pi}}\left(\frac{2}{a}\right)^{3/2} e^{-2r/a}\beta(1)$$

c) First excited states:

$$\psi_e(1) = 2s^1_{He}\alpha(1) \quad \text{or} \quad 2s^1_{He}\beta(1)$$

$$= \frac{1}{4\sqrt{2\pi}}\left(\frac{2}{a}\right)^{3/2}\left(2 - \frac{2r}{a}\right)e^{-r/a}\alpha(1)$$

$$\text{or} \quad \frac{1}{4\sqrt{2\pi}}\left(\frac{2}{a}\right)^{3/2}\left(2 - \frac{2r}{a}\right)e^{-r/a}\beta(1)$$

Q5. Helium atom with 2 non-interacting electrons:

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

a) Show that $\phi(r_1, r_2) = \phi_1(r_1)\,\phi_2(r_2)$

We want to show $\hat{H}\,\phi(r_1,r_2) = E\,\phi(r_1,r_2)$

$$\begin{aligned}
L.H.S. &\equiv \hat{H}\,\phi(r_1,r_2) \\
&= (\hat{H}_1 + \hat{H}_2)(\phi_1(r_1)\,\phi_2(r_2)) \\
&= \hat{H}_1\,\phi_1(r_1)\,\phi_2(r_2) + \hat{H}_2\,\phi_1(r_1)\,\phi_2(r_2) \\
&= \phi_2(r_2)\left(\hat{H}_1\,\phi_1(r_1)\right) + \phi_1(r_1)\left(\hat{H}_2\,\phi_2(r_2)\right)
\end{aligned}$$

By definition $\hat{H}_1\phi_1(r_1) = E_1\phi_1(r_1)$

$\hat{H}_2\phi_2(r_2) = E_2\phi_2(r_2)$

$$\begin{aligned}
&= \phi_2(r_2)\left(E_1\,\phi_1(r_1)\right) + \phi_1(r_1)\left(E_2\,\phi_2(r_2)\right) \\
&= (E_1 + E_2)\,\phi_1(r_1)\,\phi_2(r_2) \\
&= E\,\phi(r_1,r_2) \equiv R.H.S.
\end{aligned}$$

with $E = E_1 + E_2$.

5b. Ground State of 2 electron system.

Ground state configuration of Helium atom ground state is $(1s^2)$.

Since both electrons occupy the same spatial orbital (1s) therefore it forces the spin wavefunction to be anti-symmetric as in problem 3(e).

Thus:

$$\psi_g(1,2) = \left[1s(1)\,1s(2)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right].$$